US 4323684 equivalent

⑲ 日本国特許庁 (JP)　　⑪ 特許出願公開

⑫ 公開特許公報 (A)　　昭56—25185

⑤1Int. Cl.³	識別記号	庁内整理番号	⑬公開　昭和56年(1981)3月10日
C 07 D 491/113		6736—4C	
//C 08 K 5/34	CAB	6911—4J	発明の数　1
(C 07 D 491/113			審査請求　未請求
221/00			
325/00)			(全 4 頁)

⑤4 4—ピペリドンスピロケタール化合物の製造方法

⑳特　願　昭54—100916
㉒出　願　昭54(1979)8月8日

㉒発 明 者　久保田直宏
浦和市白幡1498番地アデカ・アーガス化学株式会社内
㉒発 明 者　柴田俊博
浦和市白幡1498番地アデカ・アーガス化学株式会社内
㉑出 願 人　アデカ・アーガス化学株式会社
浦和市白幡1498番地
㉔代 理 人　弁理士　羽鳥修

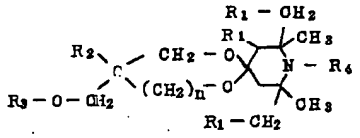
明　細　書

1. 発明の名称

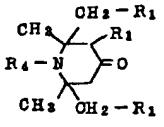
4—ピペリドンスピロケタール化合物の製造方法

2. 特許請求の範囲

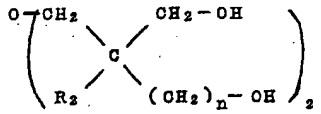
極性溶媒中で下記式〔II〕で表わされる4—ピペリドン化合物またはその酸付加塩と下記式〔III〕で表わされる多価アルコールとを反応させることを特徴とする下記式〔I〕で表わされる4—ピペリドンスピロケタール化合物またはその酸付加塩の製造方法。



〔I〕

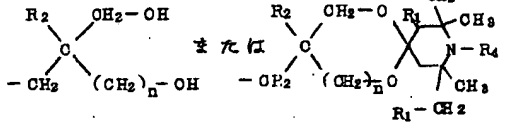


〔II〕



〔III〕

(上式中、R_1は水素原子又は炭素原子数1～4個のアルキル基を示す。R_2は水素原子、メチル基、エチル基またはヒドロキシメチル基を示す。nは0または1を示す。R_3は



を示す。R_4は水素原子又はアルキル基を示す。)

3. 発明の詳細な説明

本発明は4—ピペリドン化合物と多価アルコールとを反応させて4—ピペリドンスピロケタール化合物を製造する方法に関する。

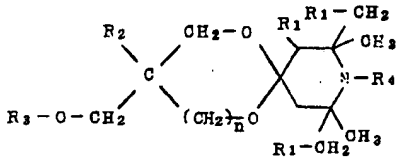
一般式〔I〕で示される4—ピペリドンケタール化合物は合成樹脂用光安定剤またはその

中間原料として極めて有用な化合物であり、特開昭53-79934号公報に記載の如く有機溶媒中で酸性触媒存在下に4-ピペリドン化合物と多価アルコールを反応させることによつて製造されていた。

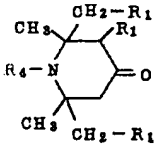
しかしながら上記方法に於て、同公報に記載の如く、有機溶媒としてトルエン/ベンゼン非極性混合溶媒系で反応を行なつた場合、多価アルコールと4-ピペリドン化合物及びその塩との親和性が低いため、反応が進行し難く、反応に長時間を要し、反応率、収率ともに低くなるという欠点を有する。

本発明者等はかかる現状に鑑み、短時間の反応で収率良く化合物〔I〕を製造する方法について鋭意検討を行なつた結果、溶媒の全部又は1部に極性溶媒を用いた溶媒中で下記式〔II〕で表わされる4-ピペリドン化合物またはその酸付加塩と下記式〔III〕で表わされる多価アルコールとを反応させると容易に反応が

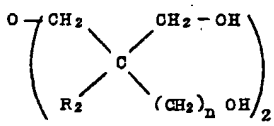
進行し、比較的短時間で収率良く下記式〔I〕で表わされる4-ピペリドンスピロケタール化合物またはその酸付加塩が製造できることを見い出し本発明に到達した。



〔I〕



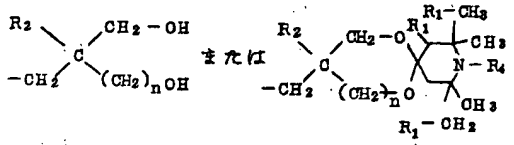
〔II〕



〔III〕

(上式中、R_1は水素原子又は炭素原子数1～4個のアルキル基を示す。R_2は水素原子、メチル基、エチル基またはヒドロキシメチル基

を示す。nは0または1を示す。R_3は



を示す。R_4は水素原子又はアルキル基を示す。)

以下、本発明をさらに詳しく説明する。

上記式〔I〕～〔III〕において、R_1で表わされるアルキル基としては、メチル、エチル、プロピル、イソプロピル、n-ブチル、sec-ブチル、t-ブチルなどがあげられる。またR_4で表わされるアルキル基としては、メチル、エチル、プロピル、ブチル、ペンチル、ヘキシル、オクチル、ベンジル、フエニルエチルなどがあげられる。

また、式〔I〕で表わされる4-ピペリドンスピロケタール化合物、または式〔II〕で表わされる4-ピペリドン化合物の酸付加塩を構成する酸としては塩酸、硫酸、リン酸、p-

トルエンスルホン酸、酢酸、シュウ酸等があげられる。

本発明の反応に用いられる極性溶媒としてはメチル-、エチル-、プロピル-、イソプロピル-、ブチル-、第2ブチル-、第3ブチル-、アミル-、第3アミル-、イソアミル-、ヘキシル-、イソヘキシル-、ヘプチル-、オクチル-、イソオクチル-、2-エチルヘキシル-、デシル-、イソデシル-、ラウリル-、トリデシルアルコール等のアルキルアルコール類；シクロペンチル-、シクロヘキシル-、シクロオクチル-、シクロドデシル-、4-メチルシクロヘキシルアルコール等のシクロアルキルアルコール類；ベンジル-、2-フエニルエチル-、3-フエニルプロピル-、2-フエニルプロピルアルコール等のアリールアルキルアルコール類；フルフリル-、テトラヒドロフルフリル-、5-メチルフルフリル-及びα-メチルフルフ

リルアルコール類；エチレングリコール、ジエチレングリコール等のグリコール類；メチルー、エチルー、イソプロピルー、ブチルー、イソブチルー、ヘキシルー、シクロヘキシルー、フエニルセロソルブ類；メチルー、エチルー、イソプロピルー、ブチルー、イソブチルカルビトール類；トリエチレングリコールモノメチルエーテル、ーモノエチルエーテル、ーモノブチルエーテル類；グリセリン、ー1,2ージメチルエーテル、ー1,3ージメチルエーテル、ー1,3ージエチルエーテル、ー1ーエチルー2ープロピルエーテル類；ホルムアミド、メチルホルムアミド、ジメチルホルムアミド（ＤＭＦ）、ジエチルホルムアミド（ＤＥＦ）、アセドアミド、メチルアセトアミド、ジメチルアセトアミド（ＤＭＡ）、Ｎーメチルピロリドン、テトラメチルウレア、ヘキサメチルホスホル（トリ）アミド等のアミド類；クロロベンゼン、Ｏージクロロベンゼン等の

ハロゲン化炭化水素類をあげることができる。これらの溶媒は1種類単独で、又は2種類以上の混合物として使用できる。

本発明の効果は上記極性溶媒のみの系でも十分に発現するが、ベンゼン、トルエン、キシレン、エチルベンゼン、キュメン、プソイドキュメン、シメン、ヘキサン、ヘプタン、オクタン、流動パラフイン、ミネラルスピリット等の炭化水素類、ジエチルエーテル、テトラヒドロフラン、ジオキサン、モノグライム、ジグライム等のエーテル類を必要に応じて溶媒の一部として用いることもできる。特にトルエン、キシレン、ヘキサン、オクタン等の炭化水素化合物は還流により、生成水を効率的に取り除くのを助けるので併用するのが好ましい。

本発明の反応を短時間で完結させるために塩酸、硫酸、リン酸、ｐートルエンスルホン酸の如き酸性触媒を用いることが好ましい。

本発明の反応は２０～３００℃、好ましくは６０～２００℃で行なわれ、また生成水を常圧または減圧下に溜去しながら行なうことが望ましい。

また本発明の反応に用いる多価アルコール、及び4ーピペリドン化合物またはその酸付加塩使用量は、必要に応じてどちらかが過剰であつても良い。

以下、実施例をもつて本発明をさらに詳しく説明するが、これにより本発明に何らの制限も加えるものではない。

比較例１－１

2,2,6,6…テトラメチル4ーピペリドン塩酸塩１９.２g（0.１０mole）、ジペンタエリスリトール１２.７g（0.０５mole）及びｐートルエンスルホン酸1.０gをトルエン９５ml及びｎーヘキサン５mlの混合溶媒に分散し、溶媒還流下生成水を除去しながら水の溜出がなくなるまで反応を行なつた。冷却後４０％

水酸化カリウム水溶液にて中和し、トルエンを加えた後、飽和食塩水にて洗浄、乾燥、脱溶媒を行なつて褐色粘稠液体１１.１g（組収率４２％）を得た。化合物の同定は次の分析結果によつた。

アミン価　理論値 5.３０％　実測値 5.２７％

I.R. ν_{NH} 3240cm^{-1}　$\nu_{C-O(ケタール)}$ 1100cm^{-1}

純度 94％（高速液体クロマトグラフイーのピーク高さ比から算出）

尚、中和後、未反応ジペンタエリスリトールを沪別、洗浄、乾燥してジペンタエリスリトール6.２gを回収した。ジペンタエリスリトールに対し反応率５１％であつた。

実施例１－１

トルエン／ｎーヘキサン（９５：５）混合溶媒のかわりにシクロヘキサノール／トルエン（９５：５）混合溶媒を用いた以外比較例１－１と全く同じ操作により反応を行ない、２４.８g（組収率９４％）を得た。

アミン価　理論値 5.30%　実測値 5.28%

I.R, ν_{NH} 3240cm^{-1} ν_{C-O}(ケタール) 1100cm^{-1}

純度 99%　反応率 99%であつた。

比較例 1-2, 1-3 実施例 1-2～1-8

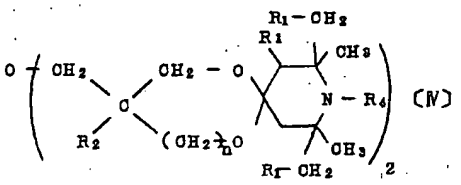
第1表に示す溶媒系により比較例1-1と全く同じ操作により反応を行なつた結果を第1表に示す。実施例に示される本発明の製造法は、反応時間、反応率、粗収率、純度において、いずれも比較例よりすぐれていることが理解される。

第 1 表

点	溶媒系（重量比）	反応時間 時間	反応温度 max℃	反応率 %	粗収率 %	純度 %
比較例						
1－1	トルエン／n－ヘキサン（95／5）	16	108	51	42	94
1－2	ベンゼン／トルエン（60／40）	17	98	54	47	95
1－3	流動パラフィン（100）	20	140	48	40	94
実施例						
1－1	シクロヘキサノール／トルエン（95／5）	1	142	99	94	99
1－2	sec－ブタノール／ヘキサン（95／5）	2	104	95	88	98
1－3	sec－ブタノール（100）	4	102	91	84	97
1－4	DMF／トルエン（60／40）	3	110	94	90	99
1－5	ブチルカルビトール／トルエン（90／10）	2	164	96	87	97
1－6	メチルセロソルブ／n－オクタン（80／20）	2	128	94	86	98
1－7	2－エチルヘキサノール／DMA／n－ヘプタン（35／35／30）	3	152	95	92	98
1－8	DEF（100）	5	181	92	88	99

実施例 2.

次の一般式〔V〕で示される第2表の化合物



〔V〕

を比較例はキシレン／トルエン（重量比90／10）混合溶媒系にて、実施例はシクロヘキサノール／トルエン（重量比90／10）系にて比較例1－1と同様な操作により反応を行なつた。

その結果を第2表に示す。

第 2 表

点	〔V〕化合物 R1	R2	R4	n	反応時間 時間	反応率 %	粗収率 %	純度 %
比較例								
2－1	H	C_2H_5	H	1	10	82	74	75
2－2	CH_3	C_2H_5	H	1	9	74	65	70
実施例								
2－1	H	C_2H_5	H	1	2	95	90	96
2－2	H	H	H	0	1	99	96	99
2－3	H	CH_2OH	CH_3	1	4	96	95	98
2－4	CH_3	C_2H_5	H	1	3	92	88	93
2－5	C_2H_5	CH_3	CH_3	1	4	95	92	93

特許出願人　アデカ・アーガス化学株式会社
代理人弁理士　羽鳥　修

United States Patent [19]

Kubota et al.

[11] **4,323,684**

[45] **Apr. 6, 1982**

equivalent to JP56-25185

[54] PROCESS FOR PREPARING A 2,2,6,6-TETRAALKYL-4-PIPERIDYL SPIRO ALIPHATIC ETHER

[76] Inventors: **Naohiro Kubota**, 404-1 Ageomura, Ageo; **Toshihiro Shibata**, 136-49-3-104 Nara-cho, Omiya, both of Japan

[21] Appl. No.: **175,487**

[22] Filed: **Aug. 5, 1980**

[30] **Foreign Application Priority Data**

Aug. 8, 1979 [JP] Japan 54-100916

[51] **Int. Cl.**³ **C07D 491/13**

[52] **U.S. Cl.** **546/19**

[58] **Field of Search** ..... 546/19; 260/45.8 NP, 260/45.8 NZ

[56] **References Cited**

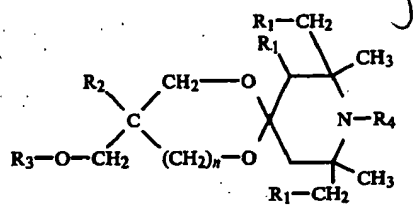
U.S. PATENT DOCUMENTS

3,899,464	8/1975	Murayama et al.	260/45.8 NP
4,096,114	6/1978	Minagawa et al.	546/19
4,105,625	8/1978	Minagawa et al.	546/19
4,115,476	9/1978	Minagawa et al.	546/19
4,116,927	9/1978	Minagawa et al.	546/16
4,118,369	10/1978	Minagawa et al.	544/224
4,124,564	11/1978	Minagawa et al.	260/45.7 R
4,128,608	12/1978	Minagawa et al.	260/45.8 NZ
4,136,081	1/1979	Minagawa et al.	546/19
4,250,312	2/1981	Nakahara et al.	546/19
4,250,313	2/1981	Nakahara et al.	546/19

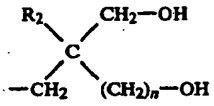
Primary Examiner—Robert T. Bond

[57] **ABSTRACT**

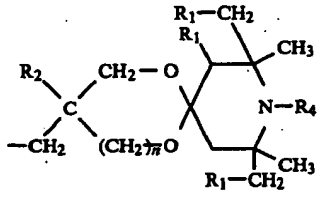
A process is provided for the preparation of a 2,2,6,6-Tetraalkyl-4-piperidyl spiro aliphatic ether represented by the formula



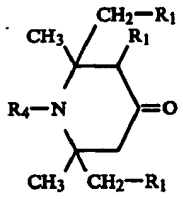
in which R_1 is a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, R_2 is a hydrogen atom, or a methyl, ethyl, or hydroxymethyl group, n is zero or one, R_3 is a group represented by a formula



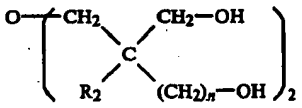
or



and R_4 is a hydrogen atom or an alkyl group, by the reaction of a 2,2,6,6-tetraalkyl-4-piperidone compound represented by the formula



or an acid addition salt thereof with an oxybis (alkanediol) compound represented by the formula



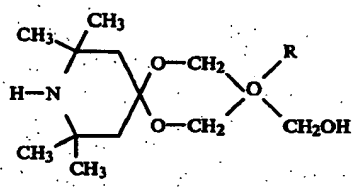
10 Claims, No Drawings

PROCESS FOR PREPARING A 2,2,6,6-TETRAALKYL-4-PIPERIDYL SPIRO ALIPHATIC ETHER

BACKGROUND OF THE INVENTION

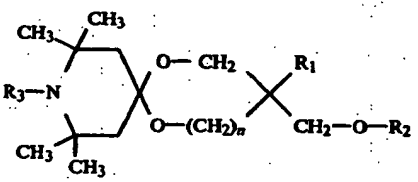
This invention relates to certain 2,2,6,6-tetraalkylpiperidine compound stabilizers for synthetic polymers and to an improved process for their preparation.

Many 2,2,6,6-tetraalkylpiperidine compound stabilizers are known. For a summary of the art, M. Minagawa et al. U.S. Pat. No. 4,124,564 of Nov. 7, 1978 can be consulted at column 1 line 15 to column 2 line 45. In particular, hindered piperidine alcohol compounds having Formula A, which can be named 2,2,6,6-tetramethyl-4-piperidone spiroketal carbinol compounds, or more systematically 9-aza-3-hydroxymethyl-3-alkyl-8,8,10,10,-tetramethyl-1,5-dioxaspiro(5,5) undecanes,


(A)

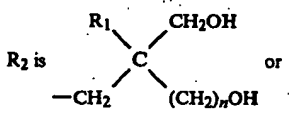
have been disclosed by K. Murayama in U.S. Pat. No. 3,899,464 of Aug. 12, 1975 as stabilizers able to protect syntheticpolymers and plastics against the harmful effects of exposure to ultraviolet radiation and heat. Compounds of Formula A have also been disclosed to be valuable synthetic intermediates for the preparation of even better stabilizers by reaction of the compounds at the alcoholic hydroxyl group to form various derivatives. Outstandingly effective stabilizers among these derivatives are certain organic phosphite esters disclosed by M. Minagawa et al in U.S. Pat. No. 4,096,114 of June 20, 1978; hydroxyaliphatic dicarboxylic and tricarboxylic acid esters disclosed by M. Minagawa et al in U.S. Pat. No. No. 4,105,625 of Aug. 8, 1978; diol bis-carbonate esters disclosed by M. Minagawa et al in U.S. Pat. No. 4,115,476 of Sept. 19, 1978; butane-and butenetricarboxylic acid esters disclosed by M. Minagawa et al in U.S. Pat. No. 4,116,927 of September 1978; heterocyclic carboxylic acid esters disclosed by M. Minagawa et al in U.S. Pat. 4,118,369 of Oct. 3, 1978; and aliphatic tetracarboxylic acid esters disclosed by M. Minagawa et al in U.S. Pat. No. 4,136,081 of Jan. 23, 1979.

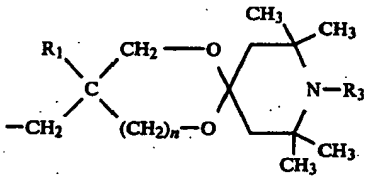
M. Minagawa et al. in U.S. Pat. No. 4,128,608 of Dec. 5, 1978 disclosed a class of 2,2,6,6-tetramethyl-4-piperidyl spiro aliphatic ether stabilizers having the general formula



wherein

R_1 is selected from the group consisting of hydrogen, lower alkyl and lower hydroxyalkyl having one or two carbon atoms;


or

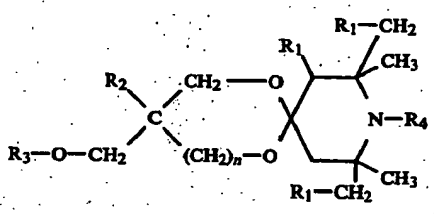


R_3 is selected from the group consisting of hydrogen and O; and n is 0 or 1.

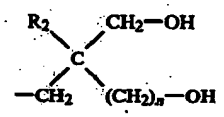
Minagawa et al. disclosed preparation of these compounds by an acidcatalyzed condensation reaction in non-polar organic solvents such as benzene and toluene.

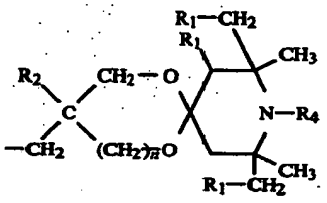
SUMMARY OF THE INVENTION

In accordance with this invention, a process for the preparation of a 2,2,6,6-tetraalkyl-4-piperidylspiro aliphatic ether represented by the formula 1

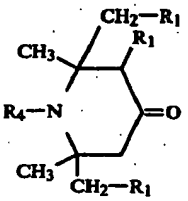

(I)

or an acid addition salt thereof, in which R_1 is a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, R_2 is a hydrogen atom, or a methyl, ethyl, or hydroxymethyl group, n is zero or one, R_3 is a group represented by a formula

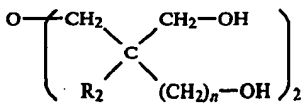

or



and R_4 is a hydrogen atom, an aralkyl group, or an alkyl group, by the reaction of a 2,2,6,6-tetraalkyl-4-piperidone compound represented by the formula 11


(II)

or an acid addition salt thereof with an oxybis(alkanediol) compound represented by the formula III



(III)

is improved in speed of reaction, yield of product, and purity of product obtained, by carrying out the reaction of the 2,2,6,6-tetraalkyl-4-piperidone compound and the oxybis(alkanediol) compound in the presence of a polar solvent selected from the group consisting of alcohols having 1 to 13 carbon atoms and 1 to 3 alcoholic hydroxyl groups, amides of phosphoric acid, carbonic acid, and carboxylic acids having 1 to 4 carbon atoms, and chlorobenzenes having 1 to 2 chlorine atoms.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the above formulas, (I), (II) and (III), the R_1 alkyl group can be methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, and t-butyl, the R_4 group can be any of these alkyls as well as pentyl, hexyl, octyl, 2-ethylhexyl, benzyl, phenylethyl, trimethylbenzyl and the like up to about 15 carbon atoms.

The acids constituting the acid addition salt of compound (I) or (II) can be hydrochloric acid, sulfuric acid, phosphoric acid, p-toluenesulfonic acid, acetic acid and oxalic acid. Many compounds represented by formula I that can be prepared by the process of this invention are disclosed by M. Minagawa et al in U.S. Pat. No. 4,128,608 of Dec. 5, 1978. The specific compounds disclosed by M. Minagawa in this patent at column 8 lines 1 to 60 are here incorporated by reference.

Exemplary polar solvents which can be used in this invention are monohydric aliphatic alcohols such as methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-amyl, tert-amyl, isoamyl, hexyl, isohexyl, heptyl, octyl, isooctyl, 2-ethylhexyl, n-decyl, isodecyl, lauryl, and tridecyl alcohols; cycloaliphatic alcohols such as cyclopentanol, cyclohexanol, cyclooctanol, cyclododecanol and 4-methylcyclohexanol; aryl substituted alcohols such as benzyl, 2-phenylethyl, 3-phenylpropyl and 2-phenylpropyl alcohols; oxygen heterocyclic alcohols such as, tetrahydrofurfuryl-, 5-methyltetrahydrofurfuryl- and α-methyltetrahydrofurfuryl-alcohol; glycols and ether-glycols such as propylene glycol, ethylene glycol and diethylene glycol; monohydric ether alcohols having 1 to 2 ether groups such as methyl, ethyl, isopropyl, butyl, isobutyl, hexyl, cyclohexyl and phenyl monoethers of ethyleneglycol and the methyl, ethyl, isopropyl, butyl and isobutyl monoethers of diethylene glycol; triethyleneglycol monoalkylethers such as triethyleneglycol-monomethylether, -monoethylether and monobutylether; glycerol derivatives such as glycerol, glycerol-1,2-dimethylether, -1,3-dimethylether, -1,3-diethylether and -1-ethyl-2-propylether; amides of phosphoric acid, carbonic acid, and carboxylic acids having 1 to 4 carbon atoms such as formamide, methylformamide, dimethylformamide (DMF), diethylformamide (DEF), acetamide, methylacetamide, dimethylacetamide (DMA), urea N-methylurea, N,N-diethylurea N,N-dimethylurea, N-methylpyrrolidone, tetramethylurea and hexamethylphosphor(tri) amide and halogenated aromatic hydrocarbons such as chlorobenzene and o-dichlorobenzene. Mixtures of these polar solvants can also be used.

The polar solvent or solvent mixture is liquid at the reaction temperature where it is used, and can be liquid or solid at room temperature. Non polar solvents can also be used together with the polar solvents. When a non-polar solvent is used, the weight ratio of polar solvent to non-polar solvent in the reaction mixture is at least 1:2, preferably at least 1:1.

Exemplary non polar solvents are hydrocarbons such as benzene, toluene, xylene, ethylbenzene, cumene, pseudocumene, cymene, hexane, heptane, octane, liquid paraffin and mineral spirit; and ethers such as diethylether, tetrahydrofuran, dioxane, 1,2-dimethoxyethane and bis(2-methoxyethyl)ether.

Water produced as a by-product of the reaction in which the spiro alkylether is produced is suitably removed as an azetrope with a hydrocarbon such as toluene, xylene, hexane and octane as the reaction proceeds. Alternatively, reaction water can be allowed to accumulate in the mixture and removed during isolation of the product.

In the process of this invention the use of an acid catalyst is preferred to complete the reaction quickly. Concentration of acid catalyst in the reaction mixture can range from about 0.01% to about 10% by weight. Suitable acid catalysts include hydrochloric acid, sulfuric acid, phosphoric acid and p-toluenesulfonic acid, and other acids having in a 1% aqueous solution a pH not greater than 3.

The process of this invention is suitably carried out at any convenient temperature in the range from 20° to 300° C., preferably in the range from 60° to 200° C.

The process of this invention can be conveniently carried out at atmospheric pressure or less than atmospheric pressure.

The invention is further illustrated without limitation by the following preparations of bis(3-hydroxymethyl-7,7,9,9-tetramethyl-8-aza-1,5-dioxa spiro (5,5)-3-undecylmethyl)ether.

CONTROL 1—1

19.2 g (0.10 mole) of 2,2,6,6-tetramethyl-4-piperidone hydrochloride, 12.7 g (0.05 mole) of dipentaerythritol and 1.0 g of p-toluenesulfonic acid were dispersed into a mixture of 95 ml of toluene and 5 ml of n-hexane and the produced water was removed under reflux for 16 hrs. Then, the reaction mixture was cooled and neutralized with 40% KOH aq.. Then toluene was added and the organic layer was washed with saturated aqueous NaCl solution, dried, and concentrated by evaporation. 11.1 g (crude yield 42%) of viscous brown oil was obtained. The compound was identified by the following analysis. Amine value: found. 5.27% calcd. 5.30% I.R.: ν_{NH}3240 cm^{-1} ν_{C-O}(ketal)1100 cm^{-1} purity: 94% (calculated from the proportion of peaks with high speed liquid chromatography) proportion of reacted dipentaerythritol: 51% (calculated from the amount of recovered dipentaerythritol)

EXAMPLE 1-1

The preparation of the 4-piperidone spiroketal alkyl ether compound as in Control 1-1 was repeated using a mixed solvent of cyclohexanol/toluene (95:5) in place of that of toluene/n-hexane (95:5). 24.8 g (crude yield 94%) of viscous brown oil was obtained.

Amine value: found. 5.28% calcd. 5.30% I.R.: ν_{NH}3240 cm^{-1} ν_{c-o}(ketal)1100 cm^{-1} purity: 99%. proportion of reacted dipentaerylthritol: 99%.

Comparison of the results of Control 1—1 and Example 1—1 according to this invention shows the unexpected and dramatic improvement brought about by use of the polar solvent in Example 1—1.

Controls 1-2, 1-3 and Examples 1-2 to 1-8

Preparations of the same 4 piperidone spiroketal alkylether as in Control 1—1 and Example 1—1 were carried out using several solvent systems in place of the solvent system of toluene/n-hexane (95:5).

The solvent systems, reaction conditions and results are shown in Table 1.

TABLE 1

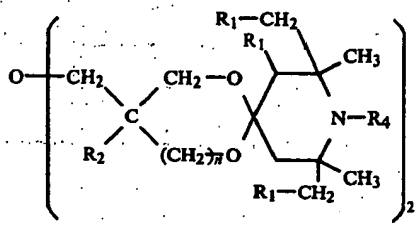
	Preparation of Bis(3-hydroxymethyl-7,7,9,9-tetramethyl-8-aza-1,5-dioxaspiro (5,5)-3-undecylmethyl) ether					
No.	Solvent system (weight ratio)	reaction time hr	reaction temperature max °C.	Proportion of reacted dipentaerythritol	Product yield (crude) %	Product purity %
Control						
1-1	toluene/n-hexane (95/5)	16	108	51	42	94
1-2	benzene/toluene (60/40)	17	98	54	47	95
1-3	liquid paraffin (100)	20	140	48	40	94
Example						
1-1	cyclohexanol/ toluene (95/5)	1	142	99	94	99
1-2	sec-butanol/ hexane (95/5)	2	104	95	88	98
1-3	sec-butanol (100)	4	102	91	84	97
1-4	DMF/toluene (60/40)	3	110	94	90	99
1-5	2(2'-butoxyethoxy)ethanol & toluene (90/10)	2	164	96	87	97
1-6	2-methoxyethanol + n/octane (80/20)	2	128	94	86	98
1-7	2-ethylhexanol/ DMA/n-heptane (35/35/30)	3	152	95	92	98
1-8	DEF (100)	5	181	92	88	99

DMF = N,N-dimethylformamide; DEF = N,N-diethylformamide

The tabulated results show the unexpected superiority of the process of this invention in giving greater yields of higher purity product in much less time than the control procedure. The results also show that the improvement obtained according to this invention is independent of the reaction temperature.

EXAMPLES 2-1 to 2-5

Several 4-piperidone spiroketal alkylether compounds having the formula (IV) were prepared.



(IV)

The compounds in Controls 2-1 to 2—2 were prepared in a mixed solvent of xylene and toluene (weight ratio (90/10) and the compounds in Examples 2-1 to 2–5 were prepared in a mixed solvent of cyclohexanol and toluene (weight ratio 90/10).

The results are shown in Table 2.

TABLE 2

	[IV] Compound							
No.	R_1	R_2	R_4	n	Reaction time hr	Proportion of reacted dipentaerythritol %	Product Yield (crude)	Product Purity %
Control								
2-1	H	C_2H_5	H	1	10	82	74	75
2-2	CH_3	C_2H_5	H	1	9	74	65	70
Example								
2-1	H	C_2H_5	H	1	2	95	90	96

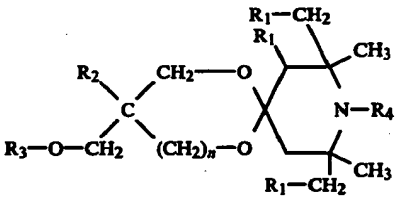
TABLE 2-continued

No.	[IV] Compound R_1	R_2	R_4	n	Reaction time hr	Proportion of reacted dipentaerythritol %	Product Yield (crude)	Product Purity %
2-2	H	H	H	0	1	99	96	99
2-3	H	CH_2OH	CH_3	1	4	96	95	98
2-4	CH_3	C_2H_5	H	1	3	92	88	93
2-5	C_2H_5	CH_3	CH_3	1	4	95	92	93

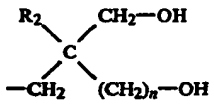
These results show the unexpected superiority of the process of this invention in the preparation of a variety of 2,2,6,6-tetraalkyl-4-piperidyl spiro aliphatic ethers in high yield and purity.

We claim:

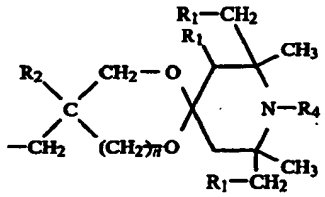
1. In a process for preparing a 2,2,6,6-tetraalkyl-4-piperidyl spiro aliphatic ether compound represented by the formula



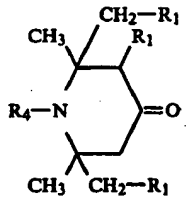
or an acid addition salt thereof, in which R_1 is a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, R_2 is a hydrogen atom, or a methyl, ethyl, or hydroxymethyl group, n is zero or one, R_3 is a group represented by a formula



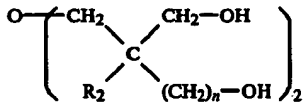
or



and R_4 is a hydrogen atom or an alkyl group, comprising the reaction of a 2,2,6,6-tetraalkyl-4-piperidone compound represented by the formula



or an acid addition salt thereof with an oxybis (alkanediol) compound represented by the formula



in which reaction water is formed, the improvement comprising carrying out the reaction of the 2,2,6,6-tetraalkyl-4-piperidone compound and the oxybis (alkanediol) compound in the presene of a polar solvent selected from the group consisting of alcohols having 1 to 13 carbon atoms and 1 alcoholic hydroxyl group, and amides of carboxylic acids having 1 to 4 carbon atoms.

2. A process according to claim 1 carried out in the presence of an acid catalyst.

3. A process according to claim 1 in which the polar solvent is a monohydric alcohol.

4. A process according to claim 3 in which the polar solvent is an aliphatic ether alcohol having 1 to 2 ether groups.

5. A process according to claim 1 in which the polar solvent is N,N-diethylformamide.

6. A process according to claim 1 in which R_1 and R_4 are hydrogen atoms.

7. A process according to claim 1 in which R_1 is a methyl or ethyl group.

8. A process according to claim 1 in which R_4 is a methyl group.

9. A process according to claim 1 in which R_2 is a methyl or ethyl group.

10. A process according to claim 1 in which R_2 is a hydroxymethyl group.

* * * * *